

Non-existence of a Hohenberg-Kohn Variational Principle in Total Current Density Functional Theory

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Abstract

For a many-electron system, whether the particle density $\rho(\mathbf{r})$ and the total current density $\mathbf{j}(\mathbf{r})$ are sufficient to determine the one-body potential $V(\mathbf{r})$ and vector potential $\mathbf{A}(\mathbf{r})$, is still an open question. For the one-electron case, a Hohenberg-Kohn theorem exists formulated with the total current density. Here we show that the generalized Hohenberg-Kohn energy functional $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H(V_0, \mathbf{A}_0) \psi(\rho, \mathbf{j}) \rangle$ can be minimal for densities that are not the ground-state densities of the fixed potentials V_0 and \mathbf{A}_0 . Furthermore, for an arbitrary number of electrons and under the assumption that a Hohenberg-Kohn theorem exists formulated with ρ and \mathbf{j} , we show that a variational principle for Total Current Density Functional Theory as that of Hohenberg-Kohn for Density Functional Theory does not exist. The reason is that the assumed map from densities to the vector potential, written $(\rho, \mathbf{j}) \mapsto \mathbf{A}(\rho, \mathbf{j}; \mathbf{r})$, enters explicitly in $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$.

I. INTRODUCTION

A cornerstone of modern density functional theory is the Hohenberg-Kohn theorem, which states that knowledge of the one-body density of a quantum-mechanical system determines the one-body potential V of the same system [1] (see also [2] for a complete proof). It has been argued [3, 4] that one can extend this theorem to a statement that knowledge of the one-body particle density plus knowledge of the one-body total current density suffices to determine the one-body potential and the magnetic vector potential for a many electron system (up to a gauge transformation). Since the proofs in [3] and [4] have been shown to contain errors (cf. [5, 6]), the existence of such a theorem remains an open question except for the one-electron case. For a system with only one electron, however, it can be shown that the particle density and the total current density determine the potentials up to a gauge transformation [5, 6]. Moreover, it is well-known that the same statement made with the paramagnetic current density in place of the total current density is not true. For instance, Vignale and Capelle [7] have constructed a counterexample that shows that different Hamiltonians can share a common ground-state for systems with magnetic fields.

In the classical Hohenberg-Kohn theory, one studies a system of N interacting electrons subjected to an electric field. Define the system's Hamiltonians to be (in suitable units)

$$H(V) = \sum_{j=1}^N (-\Delta_j + V(\mathbf{r}_j)) + \sum_{j < k} |\mathbf{r}_j - \mathbf{r}_k|^{-1}.$$

The Hohenberg-Kohn theorem then states that the particle density $\rho(\mathbf{r})$ determines the potential $V(\mathbf{r})$ up to a constant, and thereby the ground-state of $H(V)$. Let \mathcal{A}'_N be the set of particle densities having the following property: there exists a $V(\mathbf{r})$ such that $H(V)\psi = e\psi$, $\psi = \psi(\rho)$ is the unique ground-state of $H(V)$ and $\rho(\mathbf{r}) = N \int |\psi|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$.

Now, fix $V_0(\mathbf{r})$ such that $H(V_0)\psi_0 = e_0\psi_0$, where ψ_0 is the unique ground-state and $\rho_0(\mathbf{r})$ the ground-state particle density. On \mathcal{A}'_N , we can define

$$\begin{aligned} \mathcal{E}'_{V_0}(\rho) &= \langle \psi(\rho), H(V_0)\psi(\rho) \rangle = \langle \psi(\rho), H(0)\psi(\rho) \rangle + \int \rho(\mathbf{r})V_0(\mathbf{r}) \\ &= F'_{HK}(\rho) + \int \rho(\mathbf{r})V_0(\mathbf{r}), \end{aligned}$$

where the last equality defines the Hohenberg-Kohn functional F'_{HK} . The Hohenberg-Kohn

variational principle for Density Functional Theory then states that

$$e_0 = \mathcal{E}'_{V_0}(\rho_0) = \min_{\mathcal{A}'_N} \{\mathcal{E}'_{V_0}(\rho)\}.$$

The map $\rho(\mathbf{r}) \mapsto V(\mathbf{r})$, guaranteed to exist by the Hohenberg-Kohn theorem, does not enter explicitly in the functional to be minimized. Also note that ρ_0 is the unique minimizer of $F'_{HK}(\rho) + \int \rho V_0$. (To see this, assume that $\rho' \in \mathcal{A}'_N$ is another minimizer. Then there is a $V'(\mathbf{r}) \neq V_0(\mathbf{r}) + \text{constant}$, such that $H(V')$ has a ground-state ψ' with particle density ρ' . Since $V'(\mathbf{r}) \neq V_0(\mathbf{r}) + \text{constant}$, we can conclude that ψ' is not the ground-state of $H(V_0)$. But then, $e_0 < \langle \psi', H(V_0)\psi' \rangle = \mathcal{E}'_{V_0}(\rho') = e_0$, which is a contradiction.)

In this paper, we will discuss the corresponding variational principle for Current Density Functional Theory formulated with the total current density, i.e., a variational principle for an energy functional $\mathcal{E}_{V_0, \mathbf{A}_0}$ given by

$$\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H(V_0, \mathbf{A}_0)\psi(\rho, \mathbf{j}) \rangle,$$

where V_0 and \mathbf{A}_0 are the fixed scalar and vector potential, respectively. We will note the following:

- For the energy functional suggested in [3],

$$\begin{aligned} \tilde{\mathcal{E}}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) &= F_{HK}(\rho, \mathbf{j}) + 2 \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}_0(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r})(V_0(\mathbf{r}) - |A_0(\mathbf{r})|^2) d\mathbf{r} \\ &\neq \mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}), \end{aligned}$$

the counterexample in [7] shows that the densities $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ cannot satisfy a variational principle [8]. We shall here give a mathematical proof of this claim.

- For $N = 1$ and fixed potentials V_0 and \mathbf{A}_0 , the energy functional $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$ is well-defined since $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ determine $V_0(\mathbf{r})$ and $\mathbf{A}_0(\mathbf{r})$ up to a gauge transformation [5, 6]. However, $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$ can be minimized by other densities than the ground-state densities of $H(V_0, \mathbf{A}_0)$.
- For any N and under the assumption that a Hohenberg-Kohn theorem exists formulated with $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$, we show that no variational principle as that of Hohenberg-Kohn for Density Functional Theory exists for Current Density Functional Theory formulated with the total current density. This is due to the fact that the map

$(\rho, \mathbf{j}) \mapsto \mathbf{A}(\rho, \mathbf{j}; \mathbf{r})$ enters explicitly in $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$. Furthermore, this implies that $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$ cannot be extended to N -representable density pairs (ρ, \mathbf{j}) by a Levy-Lieb approach (see Section III B below).

II. NON-EXISTENCE OF A VARIATIONAL PRINCIPLE FOR $\tilde{\mathcal{E}}_{V, \mathbf{A}}$

Let $N = 1$ and consider the Schrödinger operator $H(V, \mathbf{A}) = (-i\nabla + \mathbf{A})^2 + V(\mathbf{r})$. For simplicity, we will assume that the ground-state is non-degenerate. Let H_0 denote the Schrödinger operator, when the potentials are set to zero, i.e., $H_0 = -\Delta$. For the non-degenerate ground-state ψ_0 , we compute the ground-state particle density and paramagnetic current density from $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$ and $\mathbf{j}_p(\mathbf{r}) = \text{Im}(\psi(\mathbf{r})^* \nabla \psi(\mathbf{r}))$, respectively. The total current density is then given by the sum $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r}) + \rho(\mathbf{r})\mathbf{A}(\mathbf{r})$.

For $N = 1$, a Hohenberg-Kohn theorem exists formulated with the total current density [5, 6], i.e., $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ determine $V(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ up to a gauge transformation. In particular, $\mathbf{A}(\mathbf{r}) = \mathbf{a}(\rho, \mathbf{j}; \mathbf{r}) - \nabla \chi(\mathbf{r})$ for some function $\chi(\mathbf{r})$. Denote by \mathcal{A}_1 the set of density pairs (ρ, \mathbf{j}) such that a ground-state $\psi_0 = \psi(\rho, \mathbf{j})e^{i\chi(\mathbf{r})}$ exists and fulfills

- (i) $|\psi_0|^2 = \rho(\mathbf{r})$,
- (ii) $\text{Im}(\psi_0^* \nabla \psi_0) + |\psi_0|^2 \mathbf{A}(\mathbf{r}) = \text{Im}(\psi^*(\rho, \mathbf{j}) \nabla \psi(\rho, \mathbf{j})) + |\psi(\rho, \mathbf{j})|^2 \mathbf{a}(\mathbf{r}) = \mathbf{j}(\mathbf{r})$,
- (iii) $H(V, \mathbf{A})\psi_0 = e_0\psi_0$.

On \mathcal{A}_1 , we can define the generalized Hohenberg-Kohn functional

$$F_{HK}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H_0 \psi(\rho, \mathbf{j}) \rangle. \quad (1)$$

Furthermore, for fixed $V_0(\mathbf{r})$ and $\mathbf{A}_0(\mathbf{r})$, we define on \mathcal{A}_1 , as in [3], the energy functional

$$\tilde{\mathcal{E}}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) = F_{HK}(\rho, \mathbf{j}) + 2 \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}_0(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r})(V_0(\mathbf{r}) - |A_0(\mathbf{r})|^2) d\mathbf{r}.$$

Note that $\tilde{\mathcal{E}}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) \neq \langle \psi(\rho, \mathbf{j}), H(V_0, \mathbf{A}_0)\psi(\rho, \mathbf{j}) \rangle$ on \mathcal{A}_1 . Consequently, no variational principle for the density pair (ρ, \mathbf{j}) is immediately inherited from the variational principle for the wavefunction.

The following facts follow from Theorem 4 in [6]:

- For $B < 0$ small enough and $0 < |\tilde{B}| < |B|$, there exists a wavefunction ψ_0 that is the ground-state of both $H(V, \mathbf{A})$ and $H(\tilde{V}, \tilde{\mathbf{A}})$, where $\mathbf{A}(\mathbf{r}) = (B/2) \hat{e}_z \times \mathbf{r}$ and $\tilde{\mathbf{A}}(\mathbf{r}) = (\tilde{B}/2) \hat{e}_z \times \mathbf{r}$.
- With $\varepsilon = (\tilde{B} - B)/2 > 0$ and $\mathbf{j}_\varepsilon(\mathbf{r}) = \mathbf{j}_0(\mathbf{r}) + \varepsilon(\rho_0 \hat{e}_z \times \mathbf{r})$, where ρ_0 and \mathbf{j}_0 are the ground-state densities computed from ψ_0 , it follows that $F_{HK}(\rho_0, \mathbf{j}_0) = F_{HK}(\rho_0, \mathbf{j}_\varepsilon)$ for $\varepsilon > 0$ sufficiently small.
- The density pair $(\rho_0, \mathbf{j}_\varepsilon)$ belongs to \mathcal{A}_1 for $\varepsilon > 0$ sufficiently small.

We now note that

$$\begin{aligned}\tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_\varepsilon) &= F_{HK}(\rho_0, \mathbf{j}_\varepsilon) + 2 \int \mathbf{j}_\varepsilon(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} + \int \rho_0(\mathbf{r})(V(\mathbf{r}) - |\mathbf{A}(\mathbf{r})|^2) d\mathbf{r} \\ &= \tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_0) + \varepsilon B \int \rho_0(\mathbf{r})(\hat{e}_z \times \mathbf{r})^2 d\mathbf{r},\end{aligned}$$

by the above facts. Consequently,

$$\tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_\varepsilon) - \varepsilon B \int \rho_0(\mathbf{r})(x^2 + y^2) d\mathbf{r} = \tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_0),$$

which implies $\tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_\varepsilon) < \tilde{\mathcal{E}}_{V, \mathbf{A}}(\rho_0, \mathbf{j}_0)$. Thus $\tilde{\mathcal{E}}_{V, \mathbf{A}}$ does not satisfy a variational principle.

III. NON-EXISTENCE OF A HOHENBERG-KOHN VARIATIONAL PRINCIPLE FOR TOTAL CURRENT DENSITY

A. The one-electron case

Fix $V_0(\mathbf{r})$ and $\mathbf{A}_0(\mathbf{r})$ such that $H(V_0, \mathbf{A}_0)\psi_0 = e_0\psi_0$, and let $\rho_0(\mathbf{r})$ and $\mathbf{j}_0(\mathbf{r})$ denote the ground-state densities. On \mathcal{A}_1 , we define the energy functional

$$\begin{aligned}\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) &= F_{HK}(\rho, \mathbf{j}) + 2 \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}_0(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r})(V_0(\mathbf{r}) - |\mathbf{A}_0(\mathbf{r})|^2) d\mathbf{r} \\ &\quad - 2 \int \rho(\mathbf{r}) \mathbf{A}_0(\mathbf{r}) \cdot [\mathbf{a}(\rho, \mathbf{j}; \mathbf{r}) - \mathbf{A}_0(\mathbf{r})] d\mathbf{r},\end{aligned}\tag{2}$$

where $[\mathbf{a} - \mathbf{A}] = 0$ if $\mathbf{a} - \mathbf{A} = \nabla\chi$ for some χ , and $[\mathbf{a} - \mathbf{A}] = \mathbf{a} - \mathbf{A}$ otherwise. From (ii), (2) and the definition of $F_{HK}(\rho, \mathbf{j})$, it follows that

$$\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H(V, \mathbf{A})\psi(\rho, \mathbf{j}) \rangle,$$

for $(\rho, \mathbf{j}) \in \mathcal{A}_1$. Furthermore, note that the map $(\rho, \mathbf{j}) \mapsto \mathbf{a}(\rho, \mathbf{j}; \mathbf{r})$ enters explicitly in the expression for the functional $\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j})$.

By the variational principle for the wavefunction, with $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ in \mathcal{A}_1 , we have

$$\begin{aligned}\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) &= \langle \psi(\rho, \mathbf{j}), H(V_0, \mathbf{A}_0) \psi(\rho, \mathbf{j}) \rangle \\ &\geq \langle \psi(\rho_0, \mathbf{j}_0), H(V_0, \mathbf{A}_0) \psi(\rho_0, \mathbf{j}_0) \rangle = \mathcal{E}_{V_0, \mathbf{A}_0}(\rho_0, \mathbf{j}_0) = e_0.\end{aligned}$$

Thus $e_0 = \mathcal{E}_{V_0, \mathbf{A}_0}(\rho_0, \mathbf{j}_0) = \min_{\mathcal{A}_1} \{\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})\}$. However, from the facts in Section II, it follows that the minimum of $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$ is not only achieved by the ground-state densities $\rho_0(\mathbf{r})$ and $\mathbf{j}_0(\mathbf{r})$, but also achieved by infinitely many density pairs $(\rho_0, \mathbf{j}_\varepsilon)$,

$$e_0 = \mathcal{E}_{V_0, \mathbf{A}_0}(\rho_0, \mathbf{j}_\varepsilon) = \min_{\mathcal{A}_1} \{\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})\}. \quad (3)$$

Thus, although a variational principle exists for $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$, there is no way of knowing whether a minimizer (ρ, \mathbf{j}) also is the ground-state densities of $H(V_0, \mathbf{A}_0)$.

B. Arbitrary number of electrons

Now, let $H(V, \mathbf{A})$ be the Hamiltonian of a system of N electrons and where N is arbitrary, i.e.,

$$H(V, \mathbf{A}) = \sum_{j=1}^N [(-i\nabla_j + A(\mathbf{r}_j))^2 + V(\mathbf{r}_j)] + \sum_{j < k} |\mathbf{r}_j - \mathbf{r}_k|^{-1}.$$

Under the assumption that a Hohenberg-Kohn theorem could be proven formulated with ρ and \mathbf{j} , $\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j})$ can be defined as in (2) for densities in \mathcal{A}_N . Now $F_{HK}(\rho, \mathbf{j})$ takes the form

$$\begin{aligned}F_{HK}(\rho, \mathbf{j}) &= \langle \psi(\rho, \mathbf{j}), (T + W) \psi(\rho, \mathbf{j}) \rangle, \\ T + W &= - \sum_{j=1}^N \Delta_j + \sum_{j < k} |\mathbf{r}_j - \mathbf{r}_k|^{-1},\end{aligned}$$

which agrees with (1) if $N = 1$. Here \mathcal{A}_N is the obvious generalization of \mathcal{A}_1 . As in the case $N = 1$, for $(\rho, \mathbf{j}) \in \mathcal{A}_N$, we have

$$\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H(V, \mathbf{A}) \psi(\rho, \mathbf{j}) \rangle.$$

Also, recall that the map $(\rho, \mathbf{j}) \mapsto \mathbf{a}(\rho, \mathbf{j}; \mathbf{r})$, which by assumption exists for any N , enters explicitly in the expression for $\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j})$, while in the classical Hohenberg-Kohn theory, the

corresponding map $\rho \mapsto V$ does not appear in the functional $\mathcal{E}'_V(\rho)$ (see Section I). The presence of $\mathbf{a}(\rho, \mathbf{j}; \mathbf{r})$ adds an additional layer of complexity to the generalized Hohenberg-Kohn energy functional $\mathcal{E}_{V, \mathbf{A}}$. Furthermore, in the work of Lieb [2], $F'_{HK}(\rho)$ is extended to the so called Levy-Lieb functional $F_{LL}(\rho) = \inf_{\psi} \{ \langle \psi, H(0)\psi \rangle : \psi \mapsto \rho \}$, which is defined on the set of N -representable particle densities, denoted I_N (see [2]). This extension allows the functional $F_{LL}(\rho) + \int \rho V$ to be minimized freely on the known set I_N instead of the unknown set \mathcal{A}'_N . However, even if $F_{HK}(\rho, \mathbf{j})$ could be extended to a Levy-Lieb-type functional defined for N -representable density pairs (ρ, \mathbf{j}) , no such extension is possible for $\mathcal{E}_{V, \mathbf{A}}(\rho, \mathbf{j})$ because of the term $\int \rho \mathbf{A} \cdot (\mathbf{a}(\rho, \mathbf{j}; \mathbf{r}) - \mathbf{A})$, which is by definition only meaningful for $(\rho, \mathbf{j}) \in \mathcal{A}_N$.

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